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Atty. Docket #: 1999/G-017

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE****INTERNATIONAL APPL. NO.:** PCT/EP00/05879 :**INTERNATIONAL FILING DATE:** JUNE 26, 2000:**APPLICANT:** STEFAN DISCH ET AL :**SERIAL NO:** (To be assigned) :**ART UNIT:****FILED:** -HEREWITH- :**EXAMINER:****FOR:** "LOW-EMISSION COLORED

:

POLYOXYMETHYLENE

:

MOLDING COMPOSITION"

:

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**Assistant  
Commissioner for Patents****Box PCT****Washington, D.C. 20231****\*Express Mail\* No.:** ET284671900**Date:** -FEBRUARY 05, 2002-

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to Box PCT, Commissioner for Patents, Washington, D.C. 20231

Carrie A. McPherson  
(Typed or printed name of mailing paper or fee)

Carrie A. McPherson  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS  
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371  
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1.  This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.
2.  This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.
3.  This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
4.  A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
  
5.  A copy of the International Application as filed (35 U.S.C. §371(c)(2)) --
  - a.  is transmitted herewith (required when not transmitted by International Bureau).  
  
See WIPO Publication WO 01/10952.
  - b.  has been transmitted by the International Bureau.
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US).
6.  A (verified) translation of the International Application into the English language is enclosed.
7.  Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a.  are transmitted herewith (required if not transmitted by the International Bureau).
  - b.  have been transmitted by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
  - e.  will be submitted with the appropriate surcharge.
8.  A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)(3)) is enclosed or will be submitted with the appropriate surcharge.

International Application No. PCT/EP00/05879.

9.  An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371(c)(4)) will follow.  
 and is attached to the translation of (or a copy of) the International Application.  
 and is attached to the substitute specification.

10.  A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371(c)(5)) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11.  An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.

12.  An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.

13.  A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.

14.  A substitute specification (including claims, abstract, drawing) is enclosed.

15.  A change of power of attorney and/or address letter is enclosed.

16.  Other items of information:

This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of-

22 months from the priority date under 37 CFR 1.494(c), or

32 months from the priority date under 37 CFR 1.495(c).

The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP00/05879

1999/G-017

Receiving Office: EPO  
 IPEA (if filing under 37 CFR 1.495): EPO  
 Priority Claim(s) (35 USC §§ 119, 365):  
    German Appln. 199 36 715.9 filed -August 06, 1999-.  
 A copy of the International Search Report is  
  
 enclosed.  
 attached to the copy of the International Application.  
  
 A copy of the Receiving Office Request Form is enclosed.  
 Form PTO/SB/05 (1) sheet  
 Form PCT/IB/308 (1) sheet  
 AMENDED SHEETS CLAIMS 1-6 ENGLISH AND GERMAN

The fee calculation is set forth on the next page of this Transmittal Letter.

## FEE CALCULATION SHEET

[x] A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 890.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$84 ..... -0-

Fee for multiple dependent  
claims \$280..... -0-

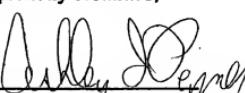
TOTAL FILING FEE... \$ 890.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By

  
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AIP/cam (5587\*327)

Enclosures

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: STEFAN DISCH *ET AL.* )  
SERIAL NO. TO BE ASSIGNED )  
FILED: HEREWITH ) ART UNIT: TO BE ASSIGNED  
FOR: LOW-EMISSION COLORED ) EXAMINER: TO BE ASSIGNED  
POLYOXYMETHYLENE MOLDING )  
COMPOSITION )  
)

Asst. Commissioner for Patents

Washington, D.C. 20231

"EXPRESS MAIL" NO. ET 284 671 900 US DATE: FEBRUARY 5, 2002

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON  
(TYPED OR PRINTED NAME OF  
PERSON MAILING PAPER OR FEE)

*Carrie A. McPherson*  
(SIGNATURE OF PERSON MAILING  
PAPER OR FEE)

PRELIMINARY AMENDMENT

Sir:

Prior to fee calculation and examination please amend the above-identified application as follows.

In the Claims

Please cancel claims 4-10.

Please add the following new claims.

- 11. The molding composition as claimed in claim 1, wherein the polyacetal copolymer comprises from 0.1 to 10 mol% of oxyethylene units.
- 12. The molding composition as claimed in claim 1, wherein the formaldehyde emission, determined on test specimens to VDA 275, is not more than 60% of the formaldehyde emission of a colored molding composition for which the polyacetal copolymer was prepared using  $BF_3$  as the initiator.
- 13. The molding composition as claimed in claim 1, wherein the formaldehyde emission, determined on test specimens to VDA 275, is not more than 20 mg/kg.

14. The molding composition as claimed in claim 1, which further comprises from 0.1 to 10% by weight of stabilizers and auxiliaries.
15. A process to prepare a molding composition which comprises preparing a polyacetal copolymer which consists essentially of oxymethylene units and oxyethylene units, using trifluoromethanesulfonic acid and/or a derivative of trifluoromethanesulfonic acid as an initiator, mixing the polyacetal copolymer with at least one colorant selected from the group consisting of white pigments, black pigments and color pigments, and obtaining a colored polyacetal molding composition whose emission of formaldehyde is lower than from a molding composition for which the polyacetal copolymer was prepared using a Lewis acid as an initiator.
16. The process as claimed in claim 15, wherein said colorant is in an amount from 0.1 to 3.0% by weight.
17. The process as claimed in claim 16, wherein the colorant carries a coating of an alkali metal salt of a fatty acid having at least 12 carbon atoms.
18. The process as claimed in claim 15, wherein the polyacetal copolymer comprises from 0.1 to 10 mol% of oxyethylene units.
19. The process as claimed in claim 15, wherein the formaldehyde emission, determined on test specimens to VDA 275, is not more than 60% of the formaldehyde emission of a colored molding composition for which the polyacetal copolymer was prepared using  $\text{BF}_3$  as initiator.
20. The process as claimed in claim 15, wherein the formaldehyde emission, determined on test specimens to VDA 275, is not more than 20 mg/kg.
21. The process as claimed in claim 15, which further comprises from 0.1 to 10% by weight of stabilizers and auxiliaries.
22. The process as claimed in claim 16, wherein the polyacetal copolymer comprises from 1.0 to 2.5 mol% of oxyethylene units.
23. The process as claimed in claim 15, wherein the formaldehyde emission, determined on

test specimens to VDA 275, is not more than 50% of the formaldehyde emission of a colored molding composition for which the polyacetal copolymer was prepared using  $\text{BF}_3$  as the initiator.

24. The process as claimed in claim 16, wherein the formaldehyde emission, determined on test specimens to VDA 275, is less than 10 mg/kg.

25. A process for reducing the formaldehyde emission of colored molding compositions made from polyacetal copolymer, which comprises preparing a polyacetal copolymer consisting essentially of oxymethylene units and oxyethylene units, using trifluoromethanesulfonic acid and/or a derivative of trifluoromethanesulfonic acid as an initiator, mixing the polyacetal copolymer with at least one colorant selected from the group consisting of white pigments, black pigments and color pigments, and obtaining a colored polyacetal molding composition whose emission of formaldehyde is lower than from a molding composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator.

26. The process as claimed in claim 25, wherein when the initiator is added in a solvent. - -

#### REMARKS

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. The applicants have rewritten claims 4-10 into proper U.S. form as newly added claims 16-26.

Claims 1-3, 8 and 11-25 are now in this case. Claims 1, 15 and 25 are the only independent claims. There are a total of 20 claims and 3 independent claims.

No additional fee is required for the claims. If there are any additional fees due in connection with the filing of this response, the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

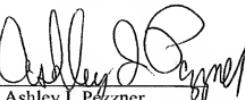
**ATTORNEY DOCKET NO.: 99/G 017 (5587\*327)**

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By



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AIP/cam  
185418

LOW-EMISSION  
COLORED POLYOXYMETHYLENE  
MOLDING COMPOSITION

Stefan Disch  
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-and-  
Lothar Reissmann

ENGLISH TRANSLATION  
OF  
INTERNATIONAL APPLICATION  
PCT/EP00/05879 . . . . . IPD: -June 26, 2000-

1999/G-017 . . . . . (5587\*327)

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SARAH L. McPherson-  
(Typed or printed name of person mailing  
paper or fee) Sarah L. McPherson  
(Signature of person mailing paper or fee)

Description

Low-emission colored polyoxymethylene molding composition

5 The present invention relates to colored polyoxymethylene molding compositions which may be used to produce low-emission colored moldings.

10 Since their introduction to the market about 35 years ago, 10 polyoxymethylenes (POMs) have become established as exceptionally useful engineering materials in a variety of applications. POMs are particularly widely used as an engineering material in automotive construction and in the electrical industry. Examples of these applications may be found in application-oriented brochures of POM producers.

15 POM copolymers and their preparation are known (Sabel et al. in Becker/Braun eds., *Kunststoff-Handbuch* [Plastics Handbook] Volume 3/1, Munich, Vienna, 1992). For example, it is known that trioxane can be copolymerized with cyclic ethers, using cationically active initiators. The 20 initiators usually used with cationic action are Lewis acids, such as  $\text{BF}_3$ , or strong protic acids, such as perfluoroalkanesulfonic acids,  $\text{HClO}_4$ , or heteropolyacids. The comonomers usually used are ethylene oxide or the cyclic formal of ethylene glycol, butanediol, or diethylene glycol.

25 It is known that the POM copolymer formed during the polymerization is suspended in a liquid protic medium to deactivate the initiator, and in the same step of the process unstable chain ends are often eliminated (DE 3703790, DE 3738632, EP 0137305). It is known that the unstable chain ends may also be degraded in homogeneous solution at from 120 to 30 220°C (*Kunststoff-Handbuch*, p. 316). Suitable solvents are water and organic solvents, in particular lower alcohols, trioxane, or dioxolane, or mixtures made from water and organic solvents. After degradation of the unstable chain ends the polymer is precipitated, washed, and dried.

35 Products made from POM copolymers have long been produced commercially and used for engineering components. A certain level of mechanical properties is required here from POM molding compositions, for example stiffness, hardness, and toughness, which is necessary if these

materials are to be used for engineering components, such as gear wheels, levers, and many others. The yield stress values published in the brochures of POM copolymer producers are from 60 to 70 N/mm<sup>2</sup>. The values which they give for the tensile modulus of elasticity of unmodified copolymers are

5 from 2400 to 3100 N/mm<sup>2</sup>. The values found for notch impact strength at 23°C are from 4 to 12 mJ/mm<sup>2</sup>.

These advantageous properties of POM molding compositions make it necessary to open up new fields of application for these materials. This

10 increasingly leads to the requirement that, besides compliance with the mechanical property profile, moldings have to have only low levels of emission of residual monomers or other volatile constituents. The automotive industry is one of the most important markets for POM products and has developed specific analysis methods for this purpose, for example  
15 15 VDA Empfehlung Nr. 275 [German Automotive Industry Recommendation No. 275], documented by Kraftfahrwesen e.V., July 1994.

The advantageous properties of polyoxymethylenes also make it necessary to extend their use to visible parts, and to open up further fields of

20 application for the material. However, a frequent requirement here is visual matching, i.e. colormatching, of the material. To this end, colorants in the form of pigments or polymer-soluble dyes are admixed with the POM molding compositions.

25 Now, it is generally known (Damm, W. and Herrmann, E., in Gächter, Müller, Plastic Additives, 3<sup>rd</sup> edition 1989, p. 730), that POM is a particular material which poses special difficulties for coloration. Because this material is sensitive to foreign substances, particularly if these are acidic or have acidic groups, as is often the case with colorants, degradation of the  
30 material with subsequent release of formaldehyde can occur during processing, and this severely limits the usefulness of the material. For the reasons mentioned it has hitherto been possible to use only a restricted number of colorants for coloring POM without impairing the properties of the material and of the product. Stabilizers are usually added to suppress  
35 degradation of the material in colored POM molding compositions. However, even the addition of stabilizers has hitherto not been able to eliminate the shortcoming of high emission levels. Many stabilizers also

impair other properties demanded from the material, for example altering the mechanical property profile, causing mold deposit, impairing high-temperature lightfastness, or giving rise to non-uniform colorant distribution.

5 Attempts have long been made to overcome these disadvantages.

JP 08208946 adds dicyandiamide as stabilizer to a pigmented polyacetal molding composition. The result is to reduce formaldehyde odor during injection molding, without loss of physical properties. However, 10 dicyandiamide is known to have a tendency toward mold-deposit formation.

JP-04077528 describes the use of POM as a carrier material for pigments. Here, nylon-6 and boric esters as dispersants are also admixed with the mixture. KR-9308188 describes the use of POM as a carrier for 15 conductivity black.

Although the use of POM as a carrier material for pigments is known, as stated above, the existing shortcoming of chemical instability and subsequent formaldehyde evolution during processing and from moldings 20 has not been satisfactorily eliminated while at the same time retaining the required property profile.

It was therefore desirable to develop colored POM molding compositions in 25 which the formaldehyde emission observed hitherto has been substantially reduced, without impairing the known advantageous properties of POM.

The object is in particular achieved by using, as base material for the colored POM molding composition, a polyacetal copolymer which is prepared using a protonic acid to initiate the polymerization.

30 The invention therefore provides a colored molding composition made from polyacetal copolymer, wherein the polyacetal copolymer essentially consists of oxymethylene units and oxyethylene units, and a strong protonic acid was used as initiator during preparation of the polyacetal 35 copolymer, and the emission of formaldehyde from the colored molding composition is lower than from a molding composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator.

The invention also provides a process for reducing the formaldehyde emission of colored molding compositions made from polyacetal copolymer, which comprises adding colorants selected from the group consisting of white pigments, black pigments, and color pigments to a 5 polyacetal copolymer which essentially consists of oxymethylene units and oxyethylene units, and using a strong protonic acid as initiator for preparing the polyacetal copolymer, and the use of the colored molding composition of the invention for producing moldings with formaldehyde emission of less than 20 mg/kg, preferably less than 10 mg/kg.

10

Surprisingly, it has been found that colored molding compositions made from POM copolymers which were prepared using strong protonic acids to initiate the polymerization have much lower emission values than those prepared from POM copolymers which were prepared using Lewis acids as 15 initiators.

The POM copolymers used as base material for the colored POM molding compositions essentially contain oxymethylene units and oxyethylene units in the polymer chain. The proportion of the oxyethylene units in the 20 structural units of the polymer chain is from 0.1 to 10 mol%, preferably from 1.0 to 2.5 mol%. The melt index MFI, measured to ISO 1133 at 190°C and 2.16 kg load, is from 1 to 75 g/10 min, preferably from 13 to 50 g/10 min, and particularly preferably from 25 to 35 g/10 min. The number-average molecular weight determined by GPC is at least 5000 g/mol and not more 25 than 100 000 g/mol.

The POM copolymers to be used according to the invention are prepared using a mixture made from trioxane and a cyclic ether or cyclic acetal, preferably dioxolane or ethylene oxide, a dialkyl formal, preferably methylal, 30 being added to the mixture to adjust the molecular weight. The amount of dialkyl formal added is from 3.4 to 34 mmol, based on the entire monomer mixture. A strong protonic acid, in particular selected from heteropolyacids, perchloric acid, and perfluoroalkanesulfonic acids, or derivatives of these, is added to the reaction mixture to initiate the polymerization. Preference is 35 given here to perfluoroalkanesulfonic acids, in particular trifluoromethanesulfonic acid. The amount of initiator is generally from 0.01 to 1.0 ppm, based on the entire monomer mixture. It is preferable to use

from 0.03 to 0.4 ppm, particularly preferably from 0.05 to 0.2 ppm, of initiator. It is advantageous to mix the initiator with an inert solvent and/or with the dialkyl formal used as chain transfer agent, and/or with the comonomer, and to use this mixture to initiate the polymerization.

5

The POM copolymer obtained during the polymerization is freed from unstable end groups by known methods, washed, and dried.

10 The colored POM molding compositions of the invention are prepared by mixing the POM copolymer with colorants and the desired stabilizers, and then pelletizing the mixture.

15 The colored POM molding compositions of the invention advantageously comprise from 90 to 99.8% by weight of POM copolymer which was prepared using a strong protonic acid or a derivative thereof as initiator, from 0.1 to 3.0% by weight of colorants, and from 0.1 to 10% by weight of selected stabilizers and auxiliaries. If required, reinforcing materials and fillers may also be admixed with the molding composition.

20 The stabilizers and auxiliaries present may be the usual additives for POM, such as antioxidants, UV stabilizers, mold-release agents, acid scavengers, nitrogen-containing costabilizers, and nucleating agents, either individually or as a mixture.

25 The colorants used may be any desired inorganic pigments, such as titanium dioxide, ultramarine blue, cobalt blue, etc., or organic pigments or colors, such as phthalocyanines, anthraquinones, etc., or carbon black, either individually or as a mixture, or together with polymer-soluble dyes. Indeed, it has been found, surprisingly, that when using the formulation of 30 the invention for the colored polyacetal molding composition, the selection of the colorants is no longer restricted to the conventional colorants particularly suitable for polyacetal, i.e. POM.

35 The colored POM molding compositions of the invention have a substantially reduced level of emission. For example, formaldehyde emission, measured on sheets of wall thickness 1 mm after 24 h of storage to VDA 275 is generally less than 20 mg/kg, preferably less than 10 mg/kg.

Some of the stabilizers usually used in POM copolymers, for example nitrogen-containing costabilizers and acid scavengers, affect formaldehyde emission. The colored POM molding compositions of the invention have substantially lower emission values than the prior art at the same level of

5 stabilization. The addition of stabilizers can therefore be reduced markedly for the colored POM molding compositions of the invention, and costs can thus be saved.

Under some circumstances, it can also be advantageous to provide the

10 colorants, prior to mixing with the polyacetal copolymer, with a coating which comprises 3% by weight or more, based on the amount of pigment, of an alkali metal salt of a fatty acid having at least 12 carbon atoms, preferably from 12 to 30 carbon atoms, for example a sodium stearate or potassium stearate. This can give a further reduction in the tendency of

15 colored polyacetal copolymers to produce emissions.

The mechanical properties of the molding compositions of the invention

comply with the usual requirements placed upon commercially available

20 POM products; they can therefore be used without restriction in the fields of

application and processing technologies which are usual for POM.

Particular fields of application for the molding compositions of the invention

are internal fittings and claddings for means of transport, such as

automobiles, aircraft, etc., household products, toys, items for babies, and

25 also devices and components for electrical engineering or electronics. The novel molding compositions are particularly suitable for producing low-emission apparatus or instruments, or parts of these, for medical applications.

### 30 Examples

The methods used to determine the properties of the material in the following examples were as follows:

35 Melt index (MFI) to ISO 1133 at 190°C and 2.16 kg load  
Tensile modulus of elasticity to ISO 527  
Yield stress to ISO 527

## Notch impact strength to ISO 179

Formaldehyde emission: Sheets of wall thickness 1 mm were manufactured from the colored POM molding compositions. After storage for 24 h, the formaldehyde emission from the sheets was determined to 5 VDA 275 (VDA Empfehlung Nr. 275 [German Automotive Industry Recommendation No. 275], documented by Kraftfahrwesen e.V., July 1994).

The results from material testing in the examples below are given in table 10 1.

The pigment mixtures used in the examples were as follows:

Pigment mixture (1): composed of 53% by weight of titanium dioxide, 39% 15 by weight of Renol black, 6.3% by weight of titanium orange, and 1.7% by weight of ekea red.

Pigment mixture (2): composed of 39.3% by weight of manganese violet VM 40, 4.4% of titanium dioxide, 54.7% of ivory black 64, 1.6% of 20 ultramarine blue 53.

## POM copolymer of the invention

96.6% by weight of trioxane, 3.4% by weight of dioxolane, and 1000 ppm of 25 methylal were charged to a batch reactor at a temperature of 80°C and a pressure of about 1 bar. 0.2 ppm of trifluoromethanesulfonic acid dissolved in 500 ppm of methylal were added to this mixture. The amounts given are based on the entire monomer mixture. After an induction time of 30 seconds, the polymerization reaction began. The crude polymer formed 30 was suspended in a water/triethylamine mixture and then hydrolyzed at 170°C in a water/methanol (10/90) mixture. On cooling to room temperature the polymer precipitated as a fine powder. The polymer was isolated by filtration with suction, washed with water, and dried.

## 35 Comparative POM copolymer

96.6% by weight of trioxane, 3.4% by weight of dioxolane, and 800 ppm of methylal were charged, the reaction conditions being as in example 1. To

this mixture were added 30 ppm of  $\text{BF}_3$ , based on the entire monomer mixture. The polymerization reaction started after an induction time of 20 s. The polymer was worked up as for the base material of the invention.

5 Example 1

The POM copolymer of the invention was mixed with 1% by weight of pigment mixture 1 and with 0.1% by weight of Licowax C (producer: Clariant AG), 0.1% by weight of calcium citrate, and 0.1% by weight of Irganox 1010. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

Example 1a

15 Example 1 was repeated except that the POM copolymer of the invention was initiated using trifluoromethanesulfonic anhydride.

Comparative Example 1

20 The comparative POM copolymer was mixed with 1% by weight of pigment mixture 1 and with antioxidant, acid scavenger, and additives, their proportions being as in example 1. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

25

Example 2

30 The POM copolymer of the invention was mixed with 1% by weight of pigment mixture 2 and with 0.1% by weight of Licowax C, 0.1% by weight of calcium citrate, and 0.1% by weight of Irganox 1010. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

35 Comparative Example 2

The comparative POM copolymer was mixed with 1% by weight of pigment mixture 2 and with antioxidant, acid scavenger, and additives, their

proportions being as in example 2. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

5

#### Example 3

The POM copolymer of the invention was mixed with 1% by weight of pigment mixture 1, and with 0.1% by weight of Licowax C, and 0.1% by weight of melamine. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

#### Comparative Example 3

15 The comparative POM copolymer was mixed with 1% by weight of pigment mixture 1 and with additives, their proportions being as in example 3. Pellets were produced from the mixture and were injection molded to give the test specimens for determining tensile modulus of elasticity, yield stress, and notch impact strength, and also to give the sheets for determining formaldehyde emission.

20

<b>Table 1</b>	Melt index g/10 min	Modulus of elasticity N/mm <sup>2</sup>	Yield stress N/mm <sup>2</sup>	Notch impact strength mJ/mm <sup>2</sup>	VDA 275* mg/kg
POM copolymer of the invention	27	-	-	-	-
Comparative POM copolymer	27	-	-	-	-
Example 1	25	2800	64	7	17
Example 1a	26	2750	66	6.5	15
Comparative Example 1	24	2920	66	6.5	43
Example 2	26	2770	64	7.5	15
Comparative Example 2	27	2890	65	7	63
Example 3	23	2770	64	7	8.5
Comparative Example 3	24	2900	66	6.5	24

\* Formaldehyde emission to VDA 275

August 6, 2001

EP0005879

11

Patent claims:

1. A process for preparing colored polyacetal compositions with reduced formaldehyde emission, which comprises preparing a polyacetal copolymer essentially consisting of oxymethylene units and oxyethylene units, using trifluoromethanesulfonic acid and/or a derivative of trifluoromethanesulfonic acid as initiator, mixing the polyacetal copolymer with at least one colorant selected from one or more of the groups consisting of white pigments, black pigments, and color pigments, and obtaining a colored polyacetal molding composition whose emission of formaldehyde is lower than from a molding composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator.  
5
- 15 2. The process as claimed in claim 1, wherein the colored polyacetal molding composition comprises from 0.1 to 3.0% by weight of colorants.
- 20 3. The process as claimed in claim 1 or 2, wherein at least one further step of the process is used to provide the colorants with a coating of an alkali metal salt of a fatty acid having at least 12 carbon atoms.
- 25 4. The process as claimed in one or more of claims 1 to 3, where the formaldehyde emission determined to VDA 275 is not more than 60%, in particular less than 50%, of the formaldehyde emission from a colored polyacetal molding composition for which the polyacetal copolymer was prepared using boron trifluoride as initiator.
- 30 5. A process for reducing the formaldehyde emission of colored molding compositions made from polyacetal copolymer, which comprises preparing a polyacetal copolymer essentially consisting of oxymethylene units and oxyethylene units, using trifluoromethanesulfonic acid and/or a derivative of trifluoromethanesulfonic acid as initiator, mixing the polyacetal copolymer with at least one colorant selected from one or more of the groups consisting of white pigments, black pigments, and color pigments, and obtaining a colored polyacetal molding composition  
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August 6, 2001

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whose emission of formaldehyde is lower than from a molding composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator.

5 6. The use of a polyacetal copolymer for preparing low-emission, colored molding compositions and moldings, wherein the polyacetal copolymer essentially consists of oxymethylene units and oxyethylene units and has been prepared using trifluoromethanesulfonic acid and/or a derivative of

10 10 trifluoromethanesulfonic acid as initiator, and the polyacetal copolymer is mixed with at least one colorant selected from one or more of the groups consisting of white pigments, black pigments, and color pigments, and the emission of formaldehyde from the colored polacetal molding composition is lower than from a molding

15 15 composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator.

1999/G017/WO

**Abstract**

Colored molding compositions made from polyacetal copolymer, where the polyacetal copolymer essentially consists of oxymethylene units and oxyethylene units, and a strong protonic acid was used as initiator during preparation of the polyacetal copolymer, have lower formaldehyde emission than that from a comparable molding composition for which the polyacetal copolymer was prepared using a Lewis acid as initiator. The formaldehyde emission is generally less than 20 mg/kg, preferably less  
5 than 10 mg/kg.  
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1999/G017 US PCT

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:  
My residence, post office address and citizenship are as stated below next to my name.  
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Low-emission pigmented polyoxymethylene molding composition**

the specification of which

(check one) is attached hereto.

was filed on  
as International Patent Application

Application Serial No. \_\_\_\_\_ and

was amended on \_\_\_\_\_ (if applicable)  
was amended through \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s) for which Priority is Claimed:**

Federal Republic of Germany, 19936715.9-43 of August 6, 1999

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

PCT/EP00/05879  
(Application Serial No.)June 26, 2000 PUB01/10952  
(Filing Date) (Status)

1999/0017 US PCT

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

18 In the matter of the above-identified application, please recognize Rudolf E. Hutz, Reg. No. 22,397; John D. Fairchild, Reg. No. 19,756; Harold Pezzner, Reg. No. 22,112; Richard M. Beck, Reg. No. 22,580; Paul E. Crawford, Reg. No. 24,397; Patricia Smink Rogowski, Reg. No. 33,791; Robert G. McMorrow, Jr., Reg. No. 30,962; Ashley I. Pezzner, Reg. No. 35,646; William E. McShane, Reg. No. 32,707; Mary W. Bourke, Reg. No. 30,982; Gerard M. O'Rourke, Reg. No. 39,794; James M. Olsen, Reg. No. 40,408; Francis DiGiovanni, Reg. No. 37,310; Eric J. Evain, Reg. No. 42,517; Daniel C. Mulveny, Reg. No. 45,897; Christine M. Hansen, Reg. No. 40,634; Patrick H. Higgins 39,709 and Elliot C. Mendelson (Agent), Reg. No. 42,878, all of P.O. Box 2207, Wilmington, Delaware 19899-2207 as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

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